CHAPTER V

RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two sections. The first section presents effect of difference Si/Ti ratio and pretreatment on physicochemical properties of TS-1. The second section reports catalytic hydroxylation reaction of benzene to phenol.

5.1 Catalyst characterization

5.1.1 XRF

Chemical compositions of synthesized catalysts were analyzed by x-ray fluorescence spectroscopy. Those results are presented in Table 5.1.

Table 5.1 Chemical compositions ratio by mole of synthesized TS-1 samples.

Sample No.	%Si	%Ti	Mole ratio of Si/Ti
1	1.5771	0.0263	60
2	1.5453	0.0386	40
3	1.5204	0.0464	32
4	1.4883	0.0674	22

5.1.2 BET

Surface areas and pore volume of each sample were measured by BET technique. The measured values of all the fresh samples are reported in Table 5.2.

Table 5.2 BET surface area of synthesized TS-1 samples

Sample no.	BET surface area (m^2/g)
1	309
2	296
3	299
4	262

From Table 5.2, the surface areas indicate that the increase amount of Ti lead to the decrease of BET surface area. This is probably because the size of titanium ion is larger than the size of silicon ion.

5.1.3 XRD

The crystallinity of the catalysts were estimated by the intensity changes of five characteristic diffraction peaks (2theta $\approx$ 7.8°, 8.8°, 23.1°, 23.8° and 24.4°) of the MFI zeolite. The results of Figure 5.2 show that all the samples behave the typical MFI structure. They have no peak at 2theta $\approx$ 25.3°, represents the anatase TiO_2 phase. Therefore, all TS-1 synthesized using TPABr as template does not contain anatase. After the catalysts were pretreated, it is found that the structures are not destroyed by the pretreatment with HNO_3.
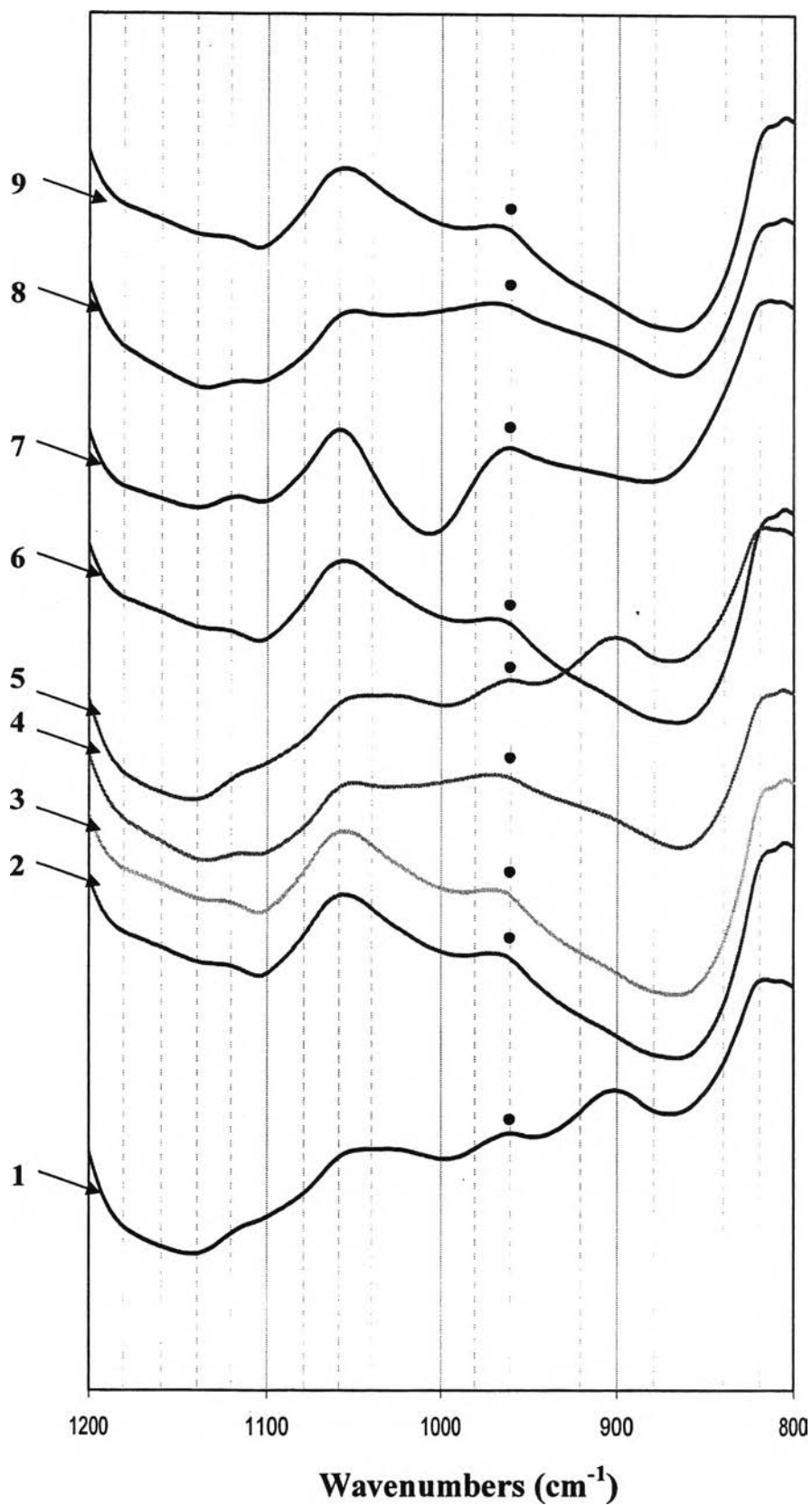
Figure 5.1 XRD patterns of TS-1 ratio60 (1), ratio40 (2), ratio32 (3), ratio22 (4) and the pretreatment with 5 M HNO$_3$ ratio60 (5), ratio40 (6), ratio32 (7), ratio22 (8) and the pretreatment with 3 M HNO$_3$ ratio40 (9).

5.1.4 FT-IR

In 2001, Li *et al.* displayed that the catalytic performance of TS-1 is related to the amount of Ti in the framework of zeolite with Si/Ti ratio in the gel decreasing, the 960 cm^{-1}band in the FT-IR spectra characterized framework titanium atoms becomes stronger. It shows more titanium atoms which are incorporated into framework. Besides, the research from Pirutko *et al.* (2001) that refer from Zecchina et al. (1991) and Bolis *et al.* (1999) displayed the IR at the position 960 cm^{-1} that is band typical for tetrahedral group Ti(OSi)$_4$ appears in the silicalite spectrum.

The IR spectra (Figure 5.2) of the synthesized TS-1 catalysts having different Si/Ti ratios show the characteristic absorption band of tetrahedral Ti^{4+} in the TS-1 framework at 960 cm^{-1}. After pretreatment with 3M HNO$_3$ (sample No.9) and 5M HNO$_3$ (sample No.5-8), it is found that the peak at about 960 cm^{-1} does not weaken, which shows framework titanium species had no been washed off by HNO$_3$.

Figure 5.2 FT-IR spectra of TS-1 ratio60 (1), ratio40 (2), ratio32 (3), ratio22 (4) and the pretreatment with 5 M HNO$_3$ ratio60 (5), ratio40 (6), ratio32 (7), ratio22 (8) and the pretreatment with 3 M HNO$_3$ ratio40 (9).

5.1.4 UV-vis

The work of Zecchina *et al.* (1991) (in Li *et al.* 2001) reported that the electronic transition involving the isolated framework Ti(IV) in the tetrahedral coordination, when characterized with UV-vis spectrocopy, could be determined by the absorption band at around 208 nm, while that involving the isolated Ti(IV) in the octahedral environment was expected at about 238 nm and the absorption band of anatase was observed at 328 nm. There are different attributions to the bands in the UV-vis spectra of Titanium Silicalite. In 2001, Li *et al.* displayed that their TS-1 synthesized using TPABr as template did not contain the anatase phase, but contained a kind of partly condensed titanium species with six-fold coordination (quasi octahedral). The titanium species may correspond to the absorption band around 270-280 nm in UV-vis spectra and this species could form $Ti-O_2^-$. This kind of $Ti-O_2^-$ was reported as a very stable form and was not a catalytic active site.

In this thesis, the preparation of catalyst (TS-1) used TPABr as template. The synthesized catalysts were also characterized by UV-vis The data from UV-vis spectrometer were analyzed using the "fityk" programme. The absorption peaks were fitted using Gaussian functions. The peak fitting results of each absorption spectrum are illustrated in Figures 5.3-5.11 and are summarized in Table 5.3.

It is found that the catalysts with ratios of Si/Ti equal to 60, 40 and 22 (samples No.1, 2 and 4, respectively) do not have any absorption peak at 328 nm [see Figures 5.3, 5.4 and 5.6]. Therefore, these samples do not contain any anatase phase. The difference is sample No.3, Si/Ti =32 [see Figure 5.5], which shows an absorption peak 328 nm, the absorption of the anatase phase [Zecchina *et al.* (1991)]. This may be because some part of the titanium of the catalyst Si/Ti = 32 forms the anatase phase rather than being incorporated into the framework of SiO_2. The peak around 270-280 nm is the signal of titanium species with six-fold coordinate. The six fold coordinate species is less reactive for the oxidation and decomposing of H_2O_2 [Li *et al.* 2001]. After all 4 catalyst samples were pretreated with 5M HNO_3 (samples No.5-8, Figures 5.7-5.10), it is found that the area of the peak at 270-280 nm obviously decreases. This shows that the pretreatment with HNO_3 can remove the six-fold coordinate titanium species, the less reactive titanium species. The results of this removal will be

discussed again in section 5.2.2. Figure 5.11 illustrates the UV-vis absorption band of the catalyst Si/Ti = 40 (sample No.2) which was pretreated with 3 M HNO_3 (sample No.9). When compare with the sample without any pretreatment (sample No.2, Figure 5.4), it is observed that the area of the absorption peak around 270-280 nm decreases slightly. This result suggests that the 3M HNO_3 solution is not an efficient solution in removing the less active six-fold coordinate titanium species. Because of this reason, no pretreatment with 3M HNO_3 was performed with the Si/Ti = 60, 32 and 22 samples.

Table 5.3 The relation between area and wavelength (nm)

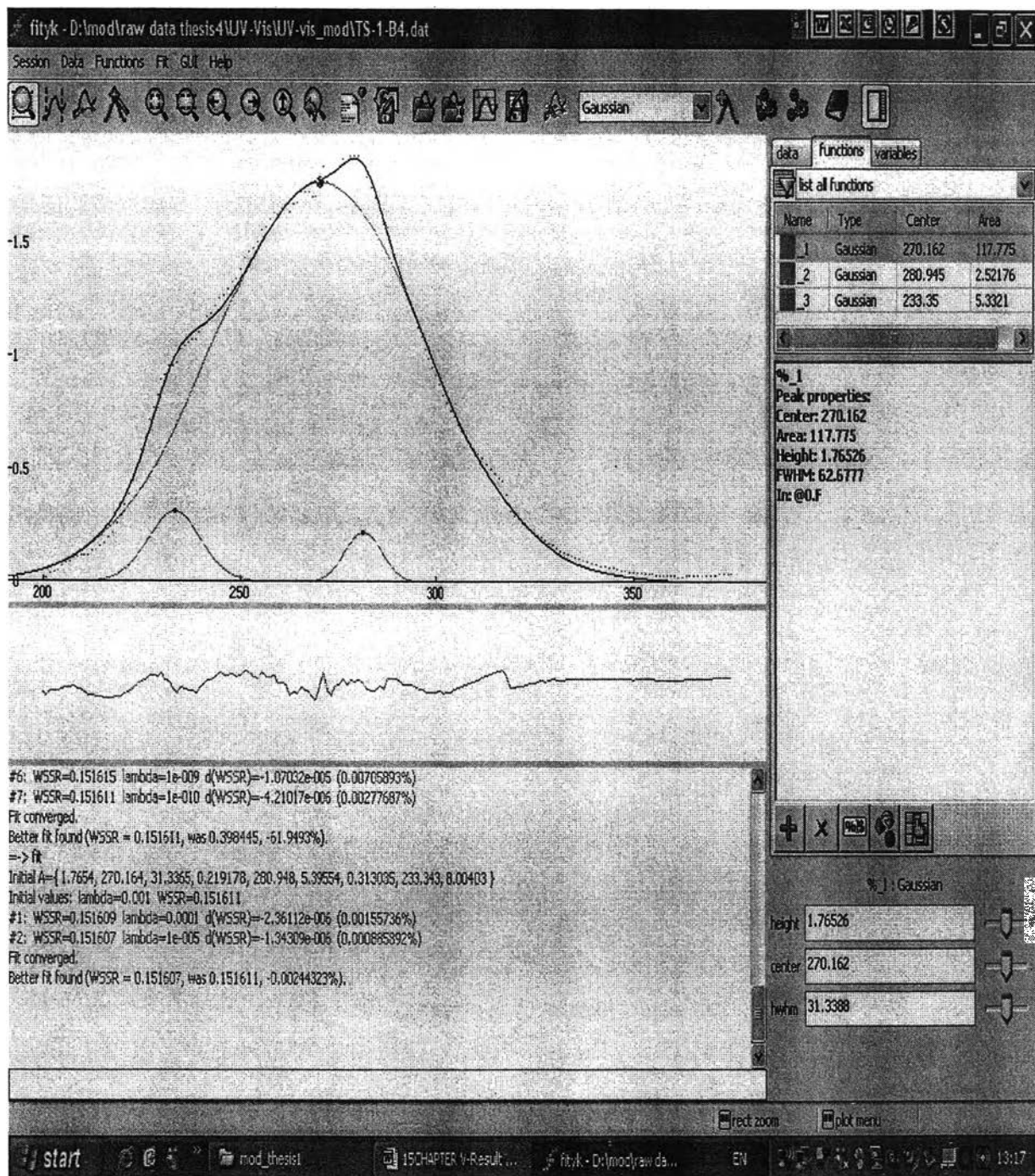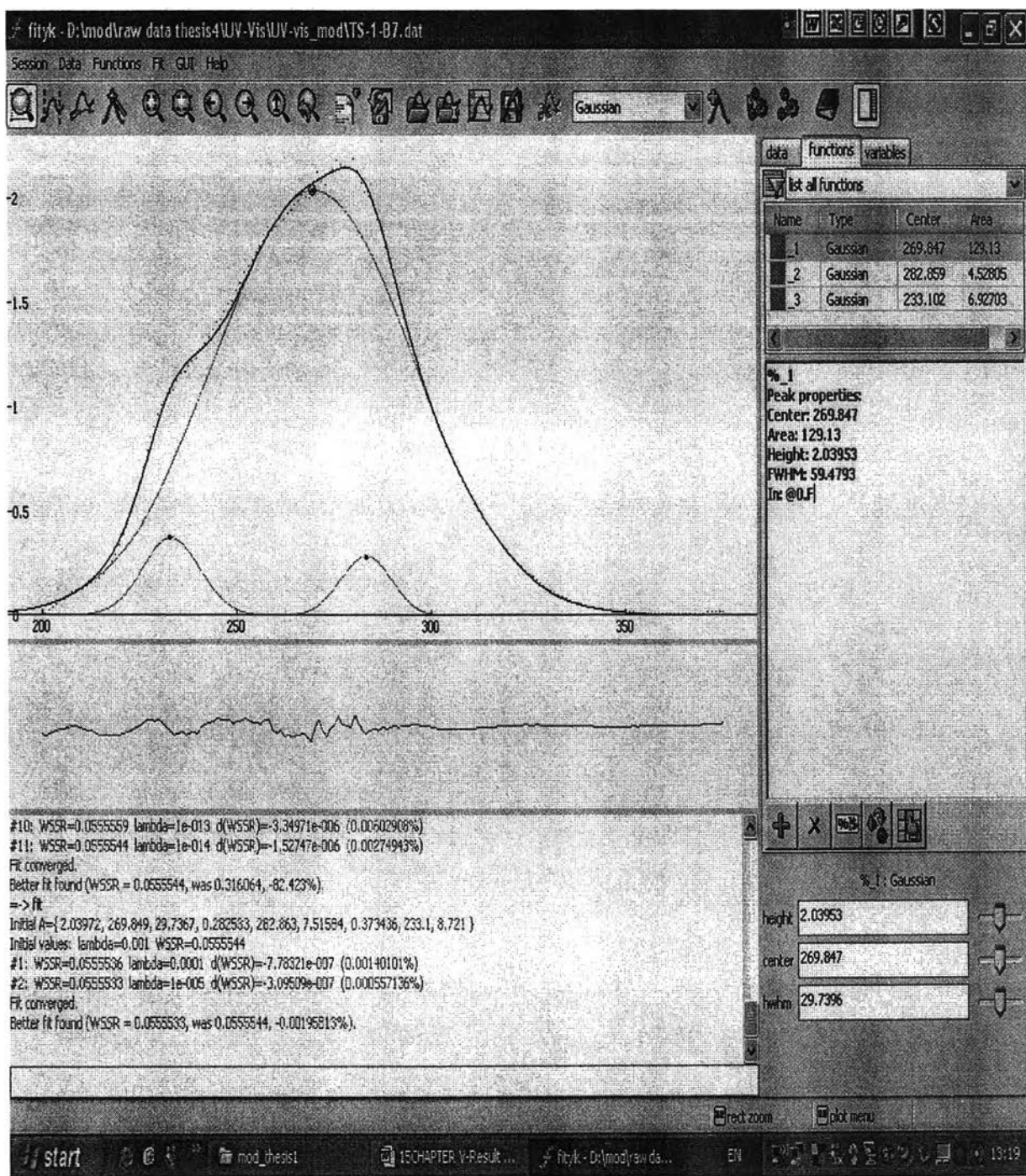| Sample No.	Wavelength (nm)	Area (a.u.)
1	233	5.33
	270	117.78
	281	2.52
2	233	6.93
	270	129.13
	283	4.53
3	233	6.41
	267	117.04
	280	5.00
4	233	6.18
	269	128.00
	285	7.19
5	230	4.32
	243	5.37
	273	66.69
6	233	4.93
	267	115.09
	277	3.94
7	230	4.92
	244	5.16
	273	65.69
8	235	12.35
	275	38.40
	-	-
9	231	5.76
	262	122.28
	274	5.95

Figure 5.3 The data of peak fitting of Si/Ti = 60 as sample No.1 in table 5.3

Figure 5.4 The data of peak fitting of Si/Ti = 40 as sample No.2 in table 5.3
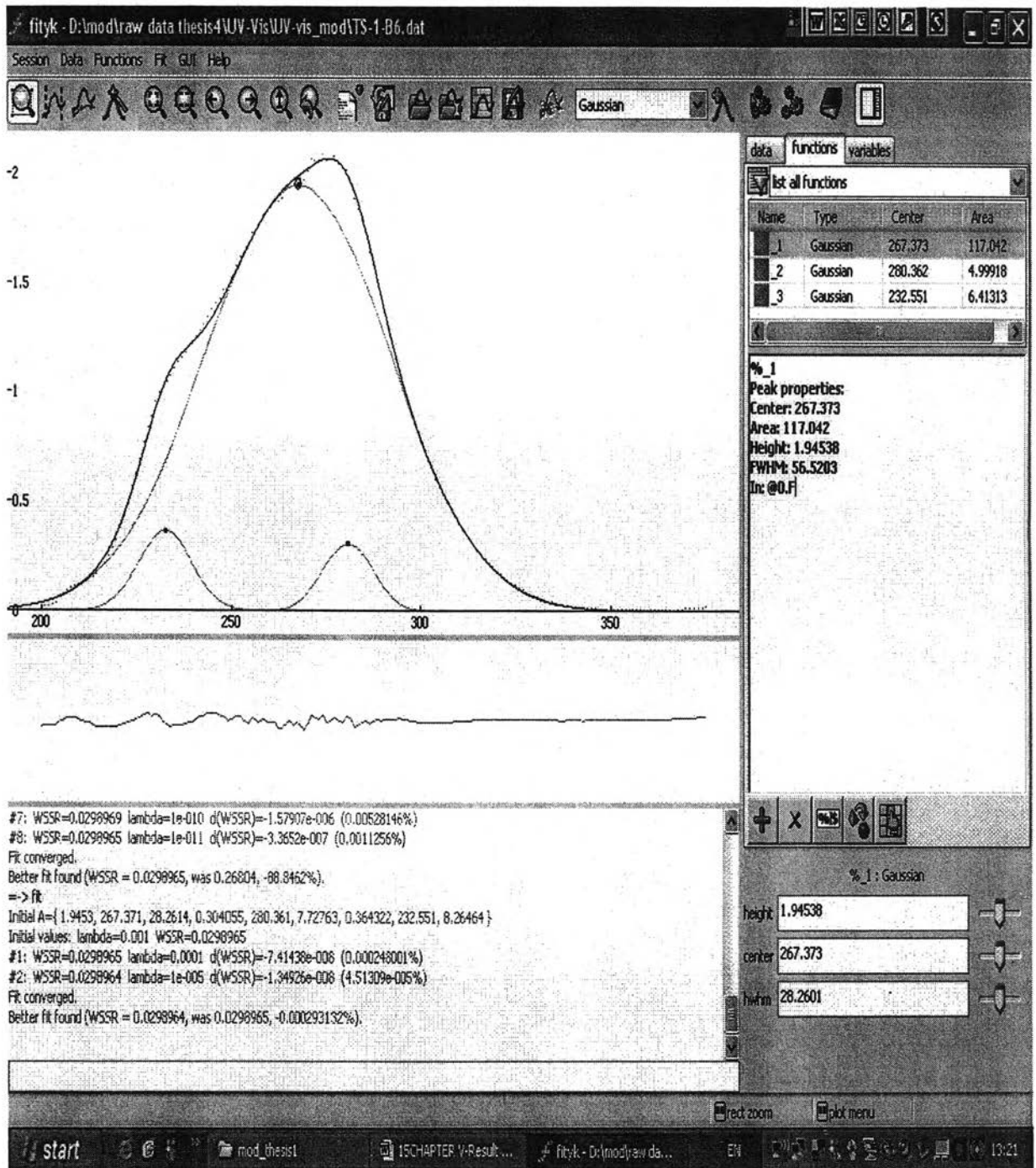
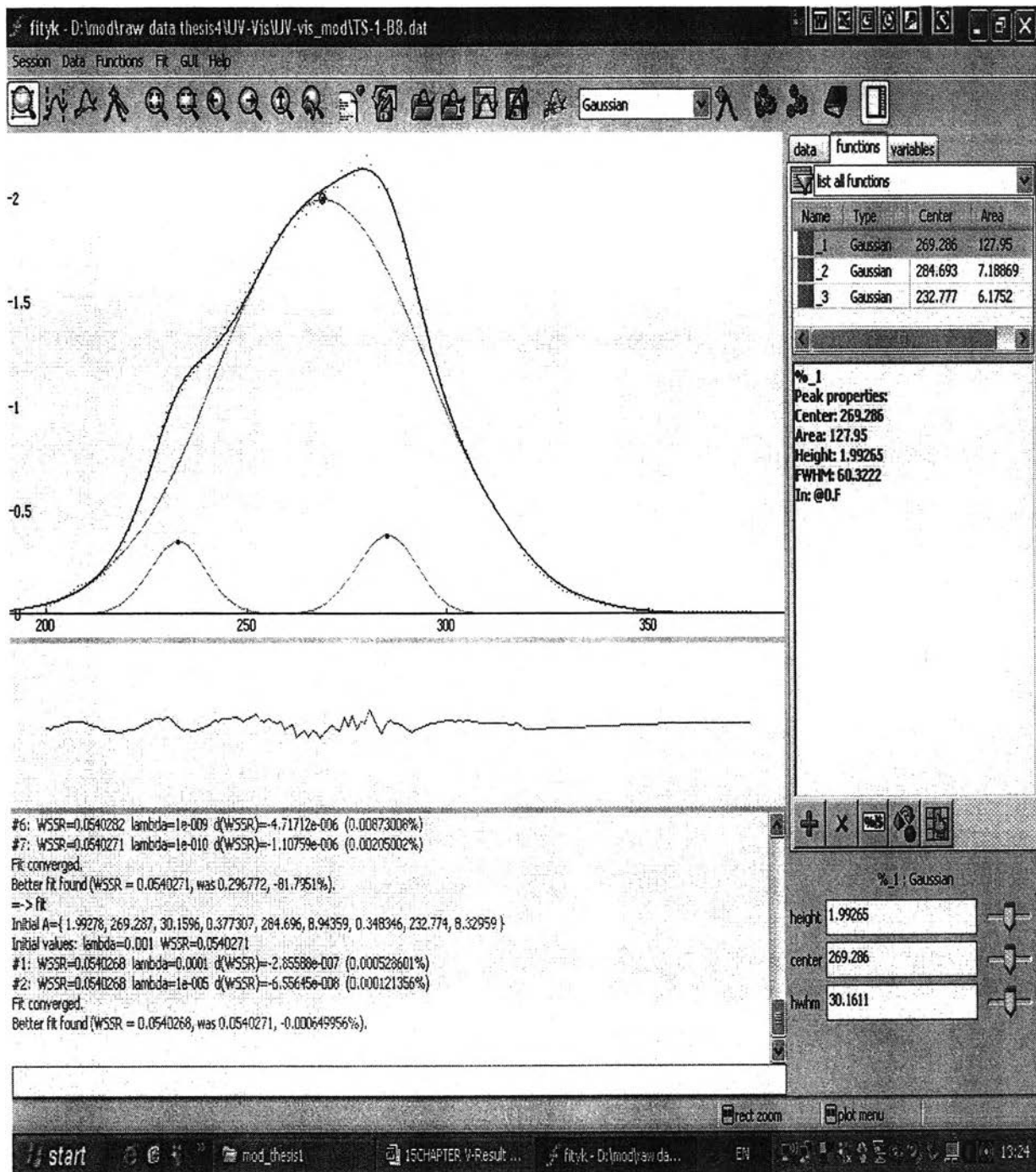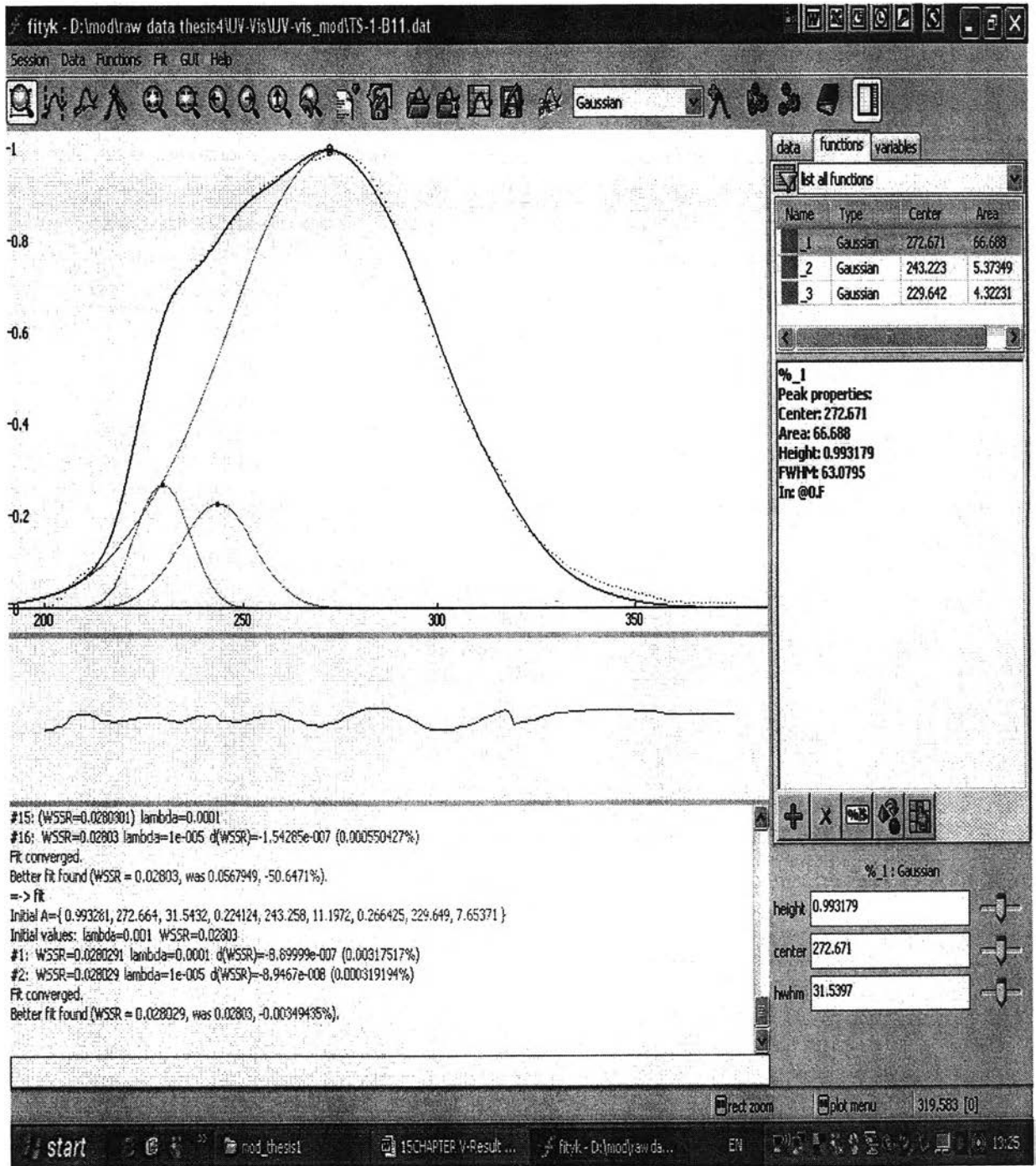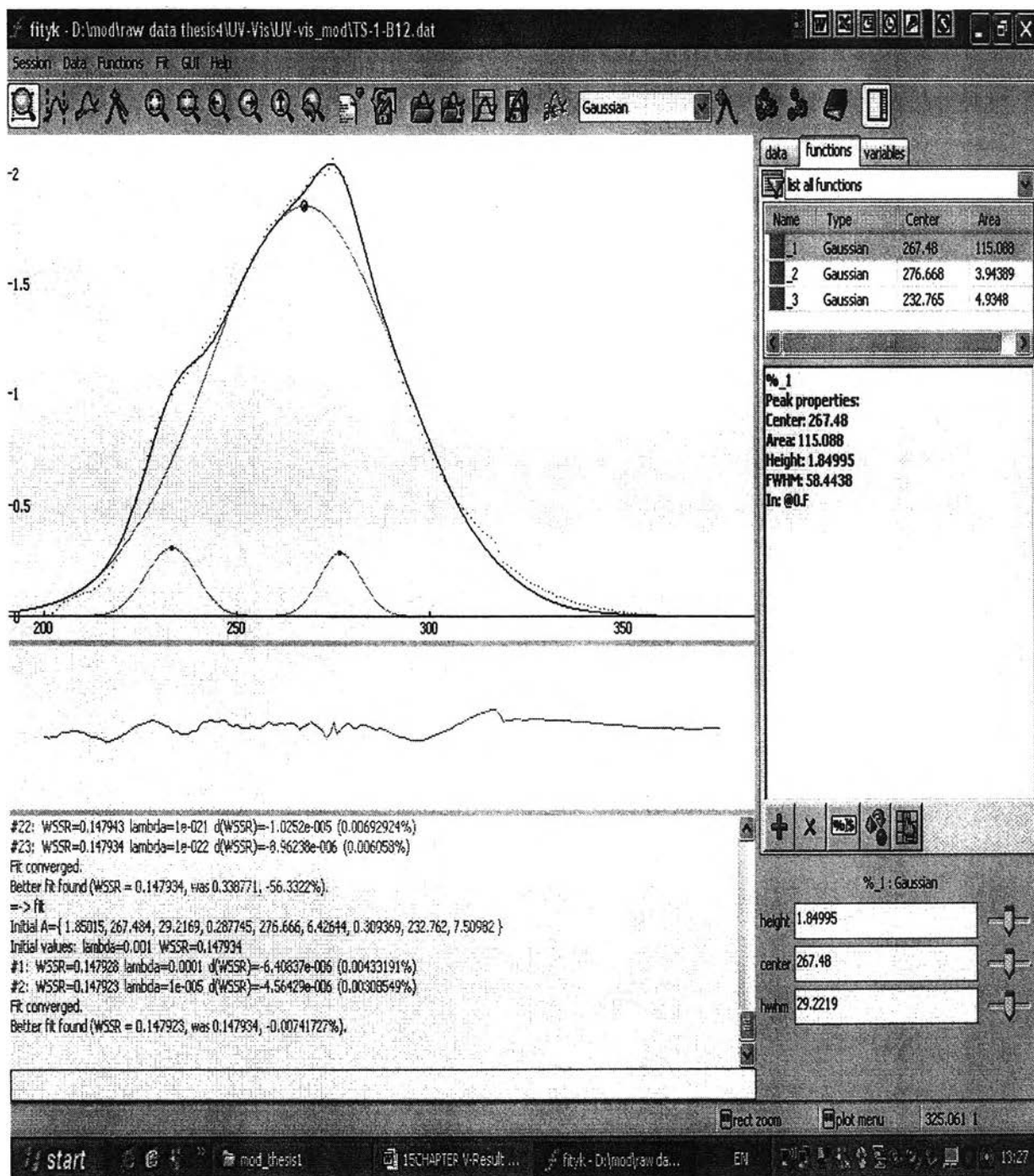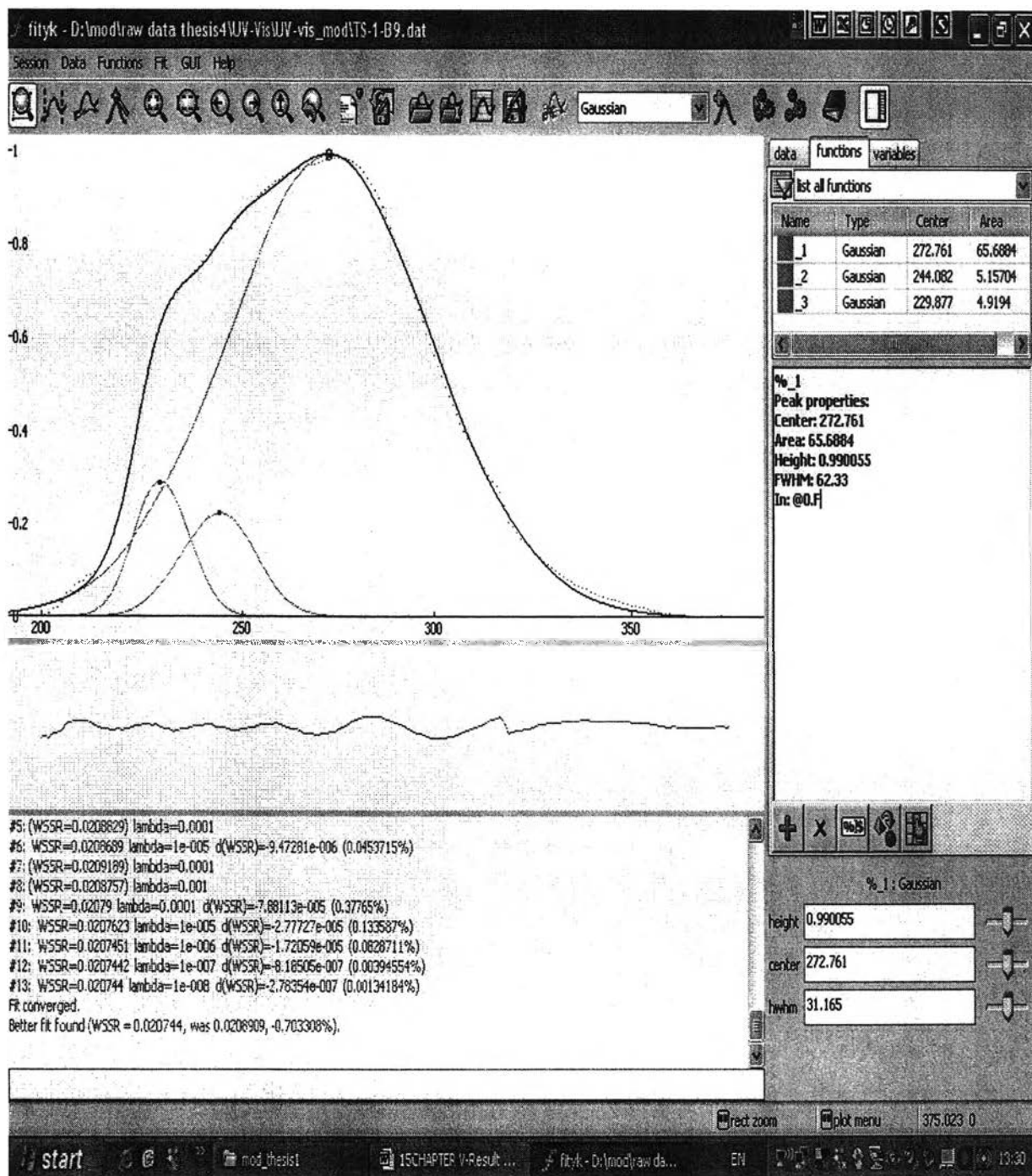**Figure 5.5** The data of peak fitting of Si/Ti = 32 as sample No.3 in table 5.3

Figure 5.6 The data of peak fitting of Si/Ti = 22 as sample No.4 in table 5.3

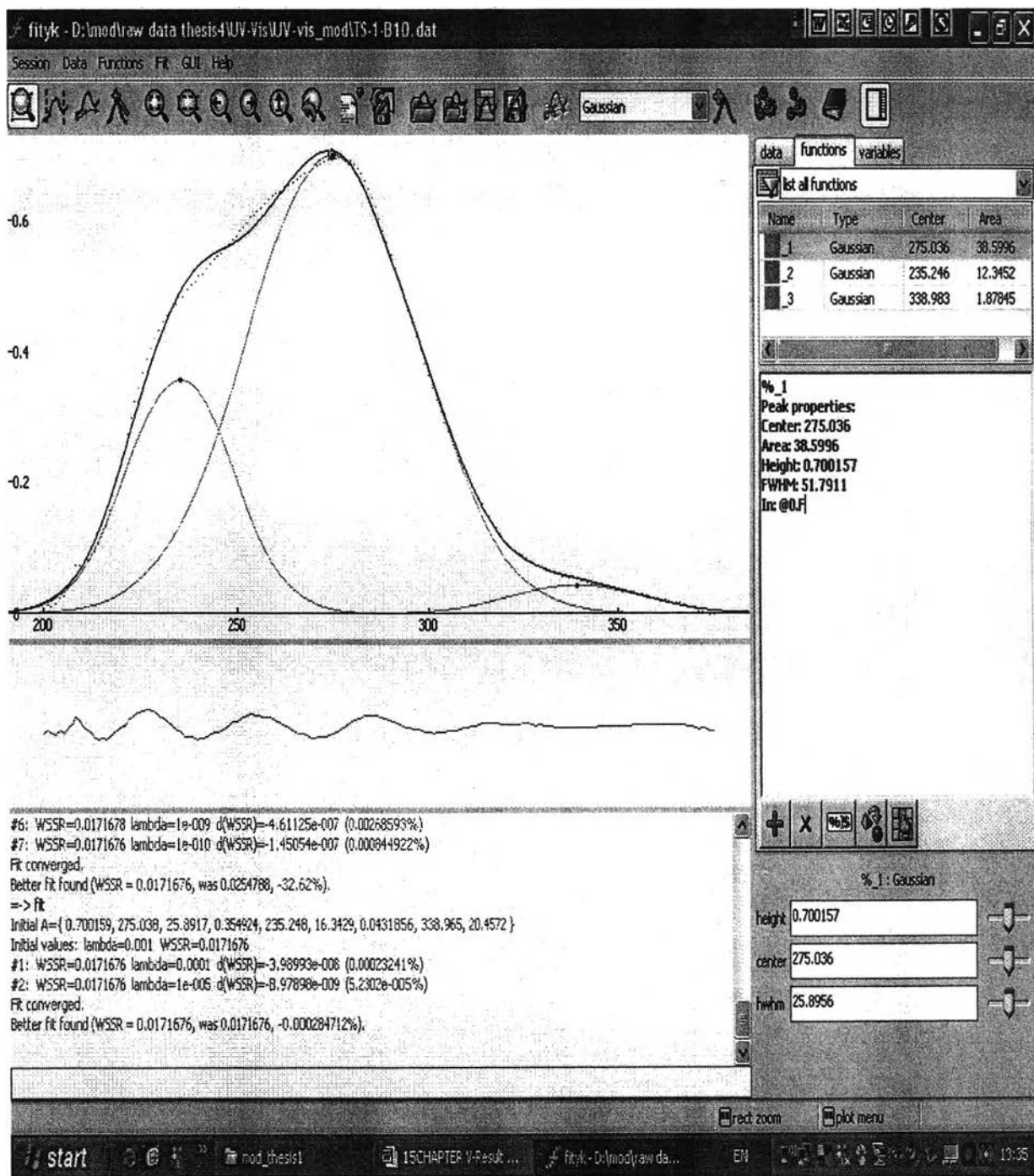**Figure 5.7** The data of peak fitting of Si/Ti = 60 that pretreated with 5M HNO$_3$ as sample No.5 in table 5.3

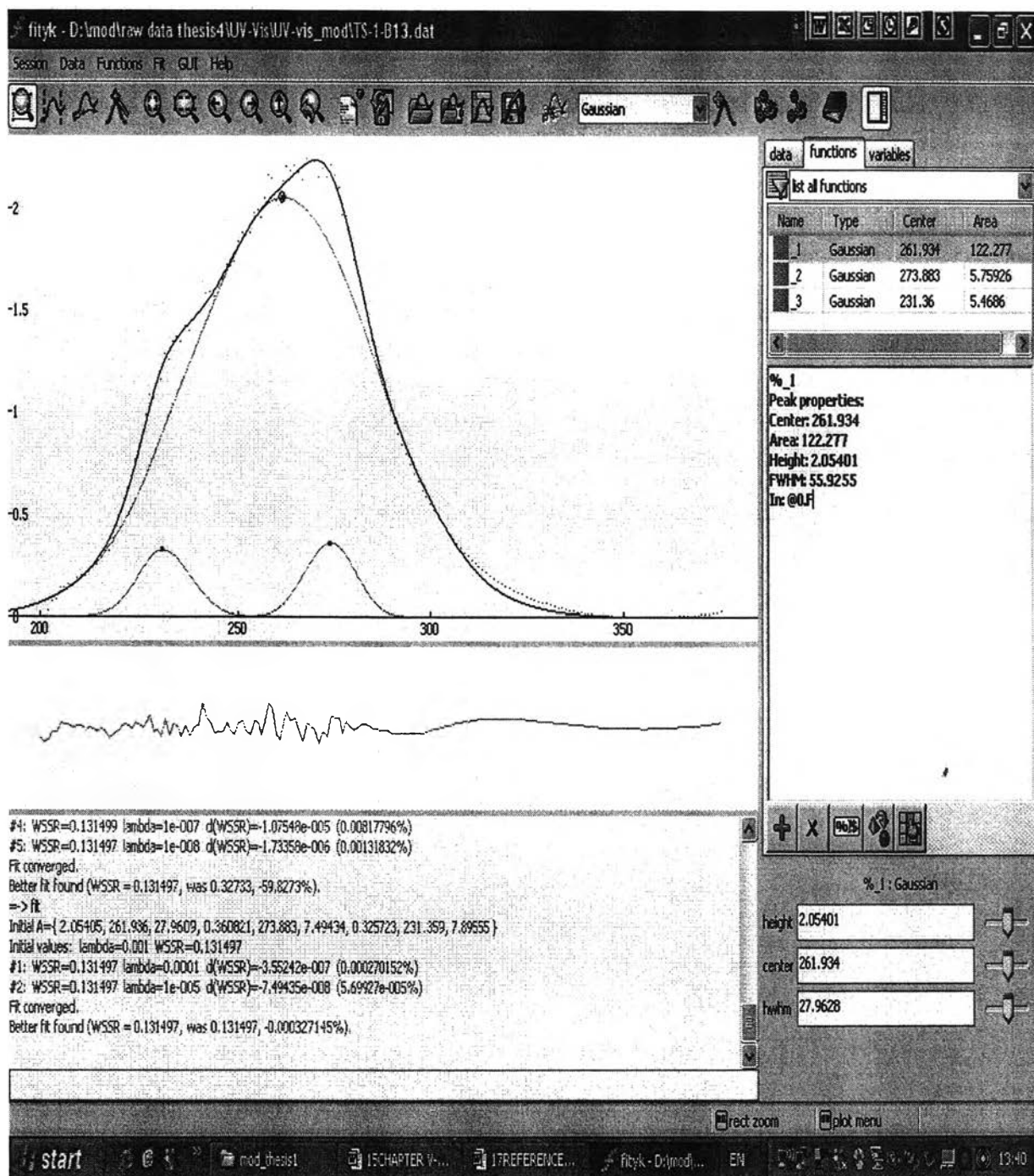**Figure 5.8** The data of peak fitting of Si/Ti = 40 that pretreated with 5M HNO₃ as sample No.6 in table 5.3

Figure 5.9 The data of peak fitting of Si/Ti = 32 that pretreated with 5M HNO₃ as sample No.7 in table 5.3

Figure 5.10 The data of peak fitting of Si/Ti = 22 that pretreated with 5M HNO₃ as sample No.8 in table 5.3

Figure 5.11 The data of peak fitting of Si/Ti = 40 that pretreated with 3M HNO₃ as sample No.9 in table 5.3

5.1.6 NH₃-TPD

NH₃-TPD was used to determine the strength and amount of the acid site of the catalysts. The results are shown in Figures 5.12-5.20 and Table 5.4. Deconvolution details of the catalyst sample without any pretreatment are shown in Figures 5.12-5.15 while Figures 5.16-5.20 illustrate the deconvolution details of the catalysts after the pretreatment. The deconvolution is performed by using a freeware programme named "fityk". The peak fitting process was carried out by finding the best fit of skew-Gaussian peak(s) (parameter "splitGaussian" in the programme). The amount of each acid site can be determined from the percentage of each component peak and the total amount of ammonia desorps. The results which are calculated from the raw data are showed in appendix B.

It is found that each NH₃-TPD profile can be deconvoluted into two main peaks. The first peak, will be named here "the weak acid site", appears around 120-145°C. The second peak, will be named here "the strong acid site", appears around 220-240°C. There are two exceptions, the profile of Si/Ti = 40 after the pretreatment with 5M HNO₃ and the profile of Si/Ti = 32, also, after the pretreatment with 5M HNO₃. Both two profiles, though, mathematically can be separated into the sum of two Gaussian peak, the locations of both peaks are about the same. Thus, practically, these two profiles should be considered as only one peak.

The results of samples No.1-4 showed in Table 5.4 indicates that the quantities of the acid site are not much different though the catalysts have different Si/Ti ratio. After the catalysts were pretreated with the aqueous solution of 5M HNO₃, the acid strength (which can be determined from the location of the peak) on the surface of the TS-1 catalyst change slightly, but the amount of acid site (the area under the peak) decrease significantly. The decrease can be attributed to the removal of the six-fold coordination species of titanium.
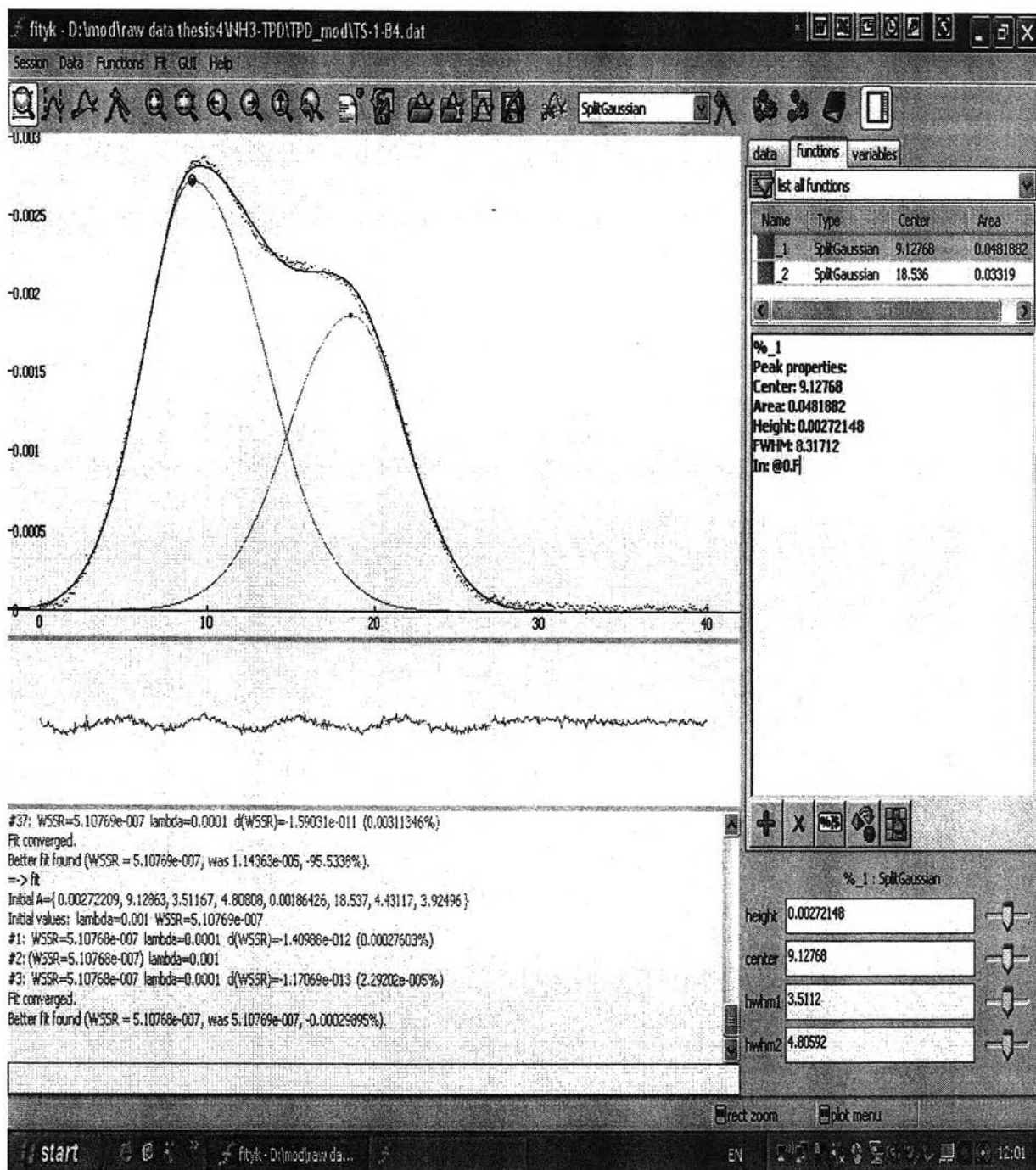
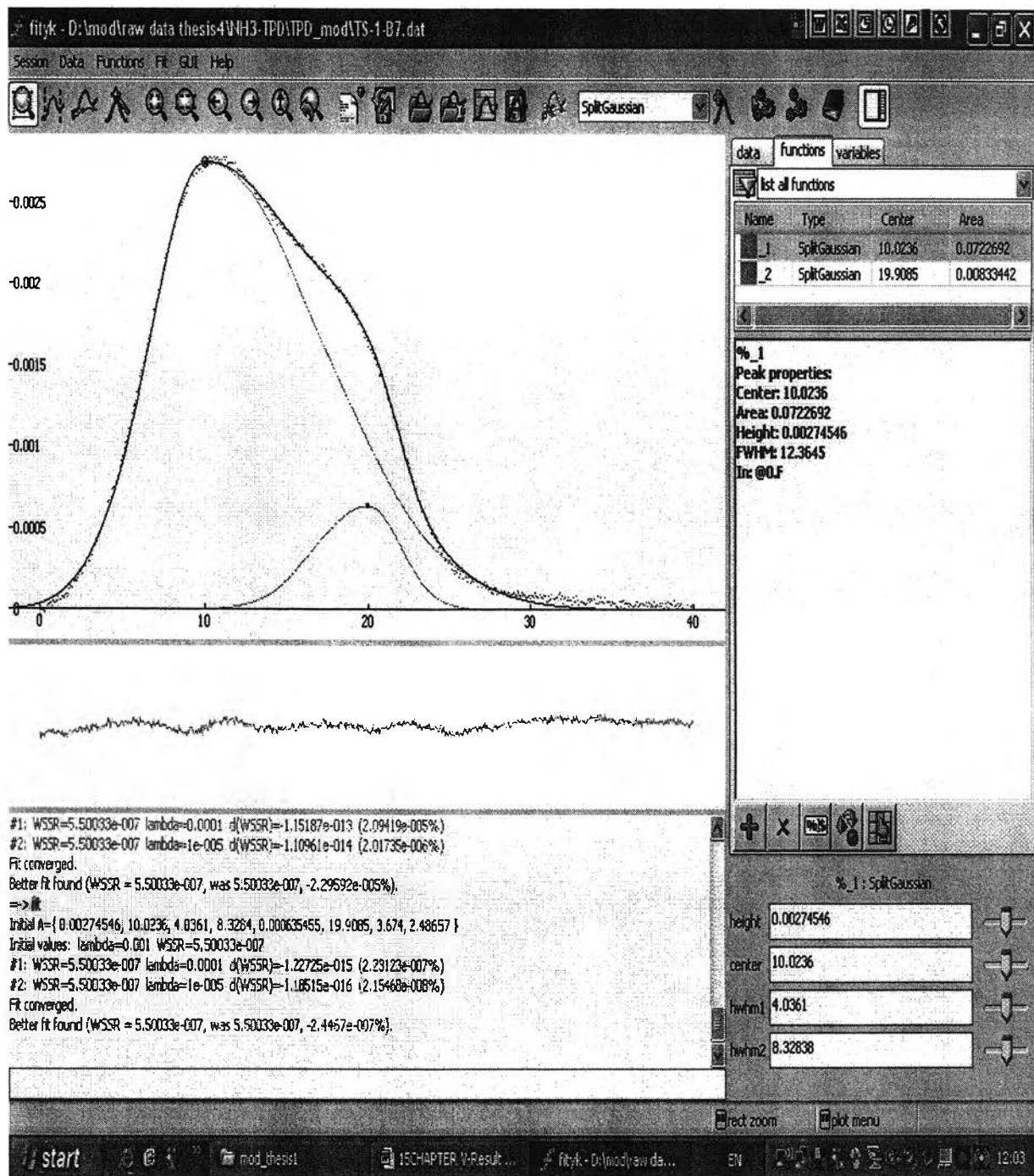**Figure 5.12** The data of peak fitting of Si/Ti = 60 as sample No.1 in table 5.4
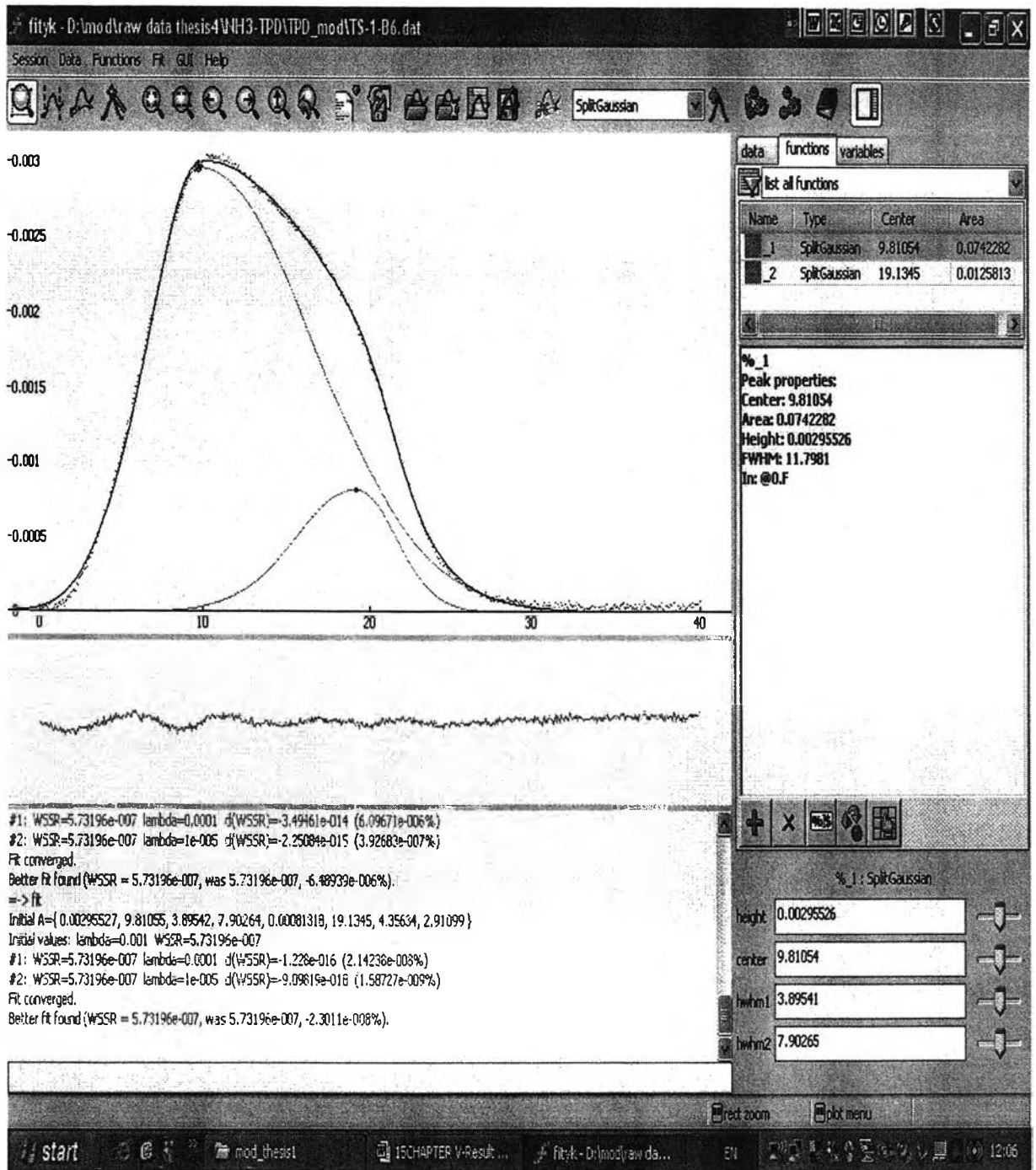
Figure 5.13 The data of peak fitting of Si/Ti = 40 as sample No.2 in table 5.4

Figure 5.14 The data of peak fitting of Si/Ti = 32 as sample No.3 in table 5.4
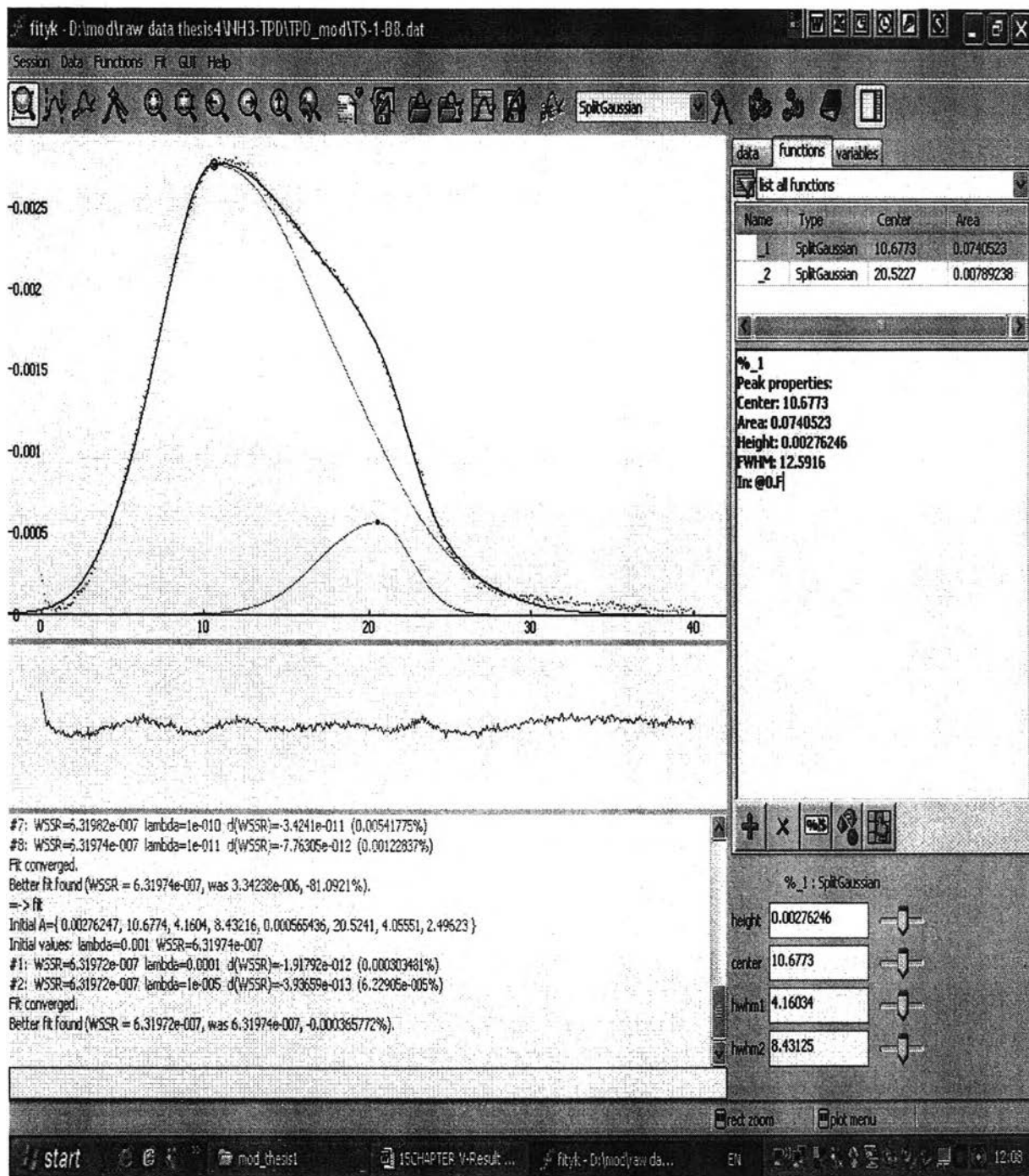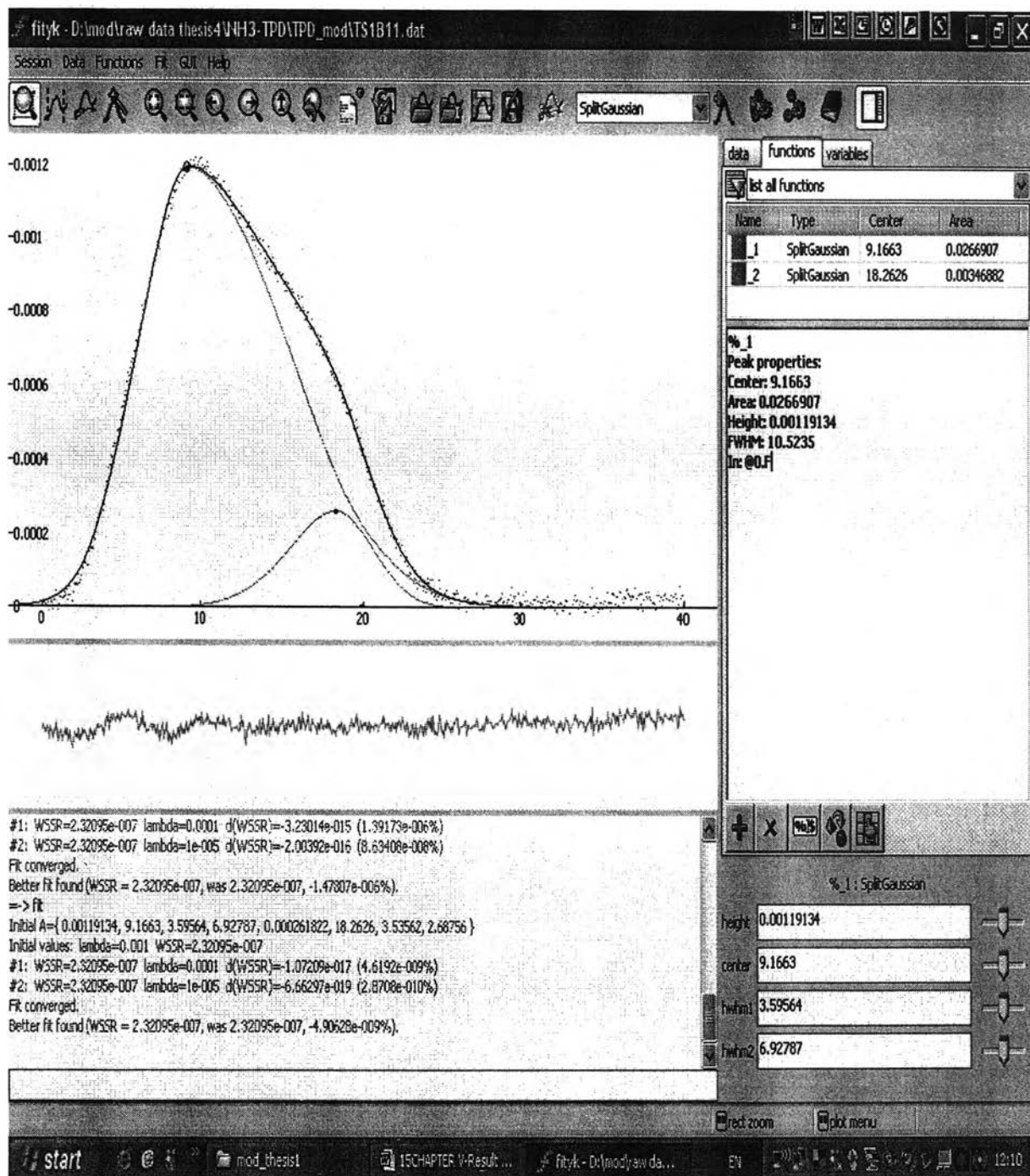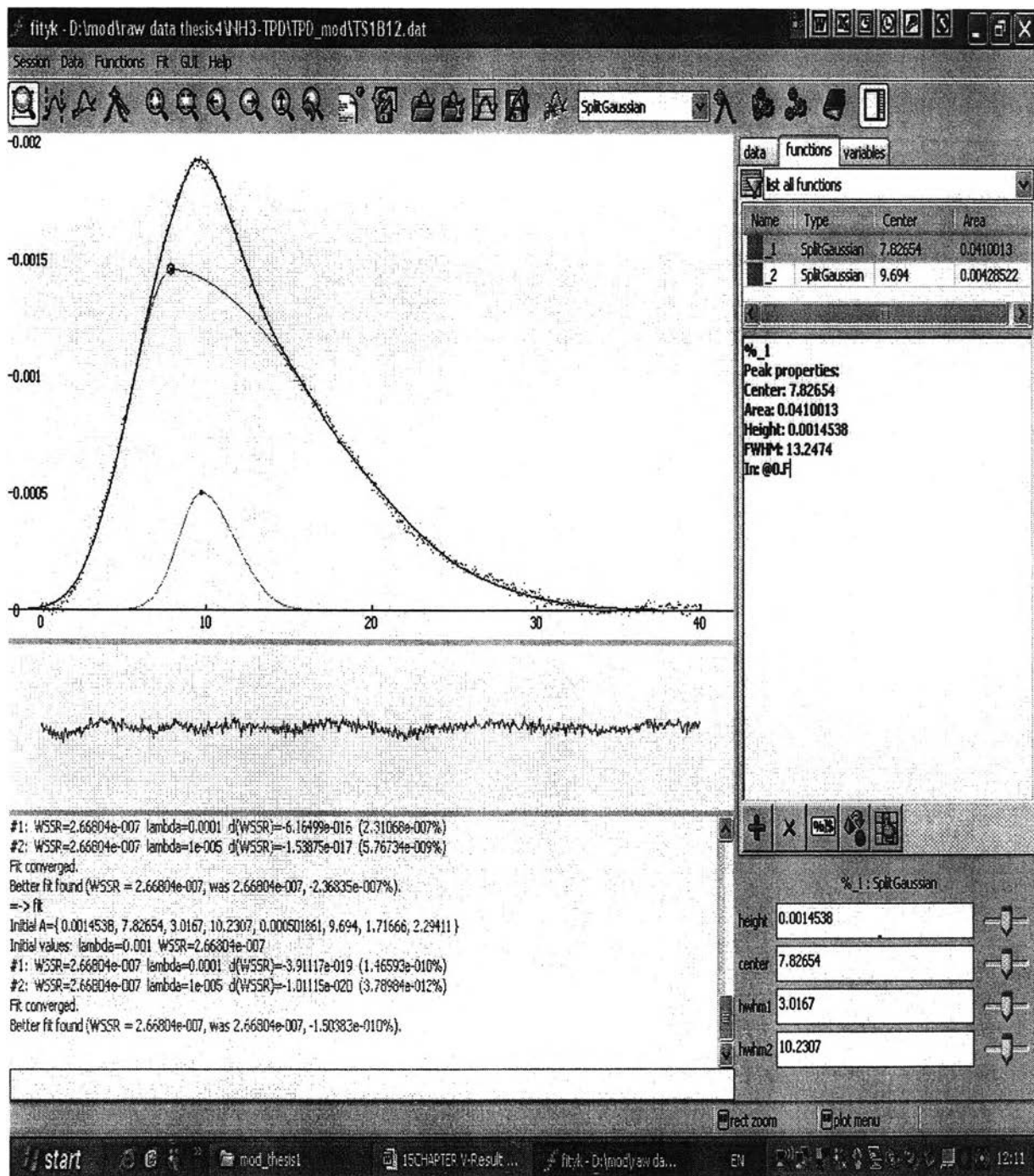
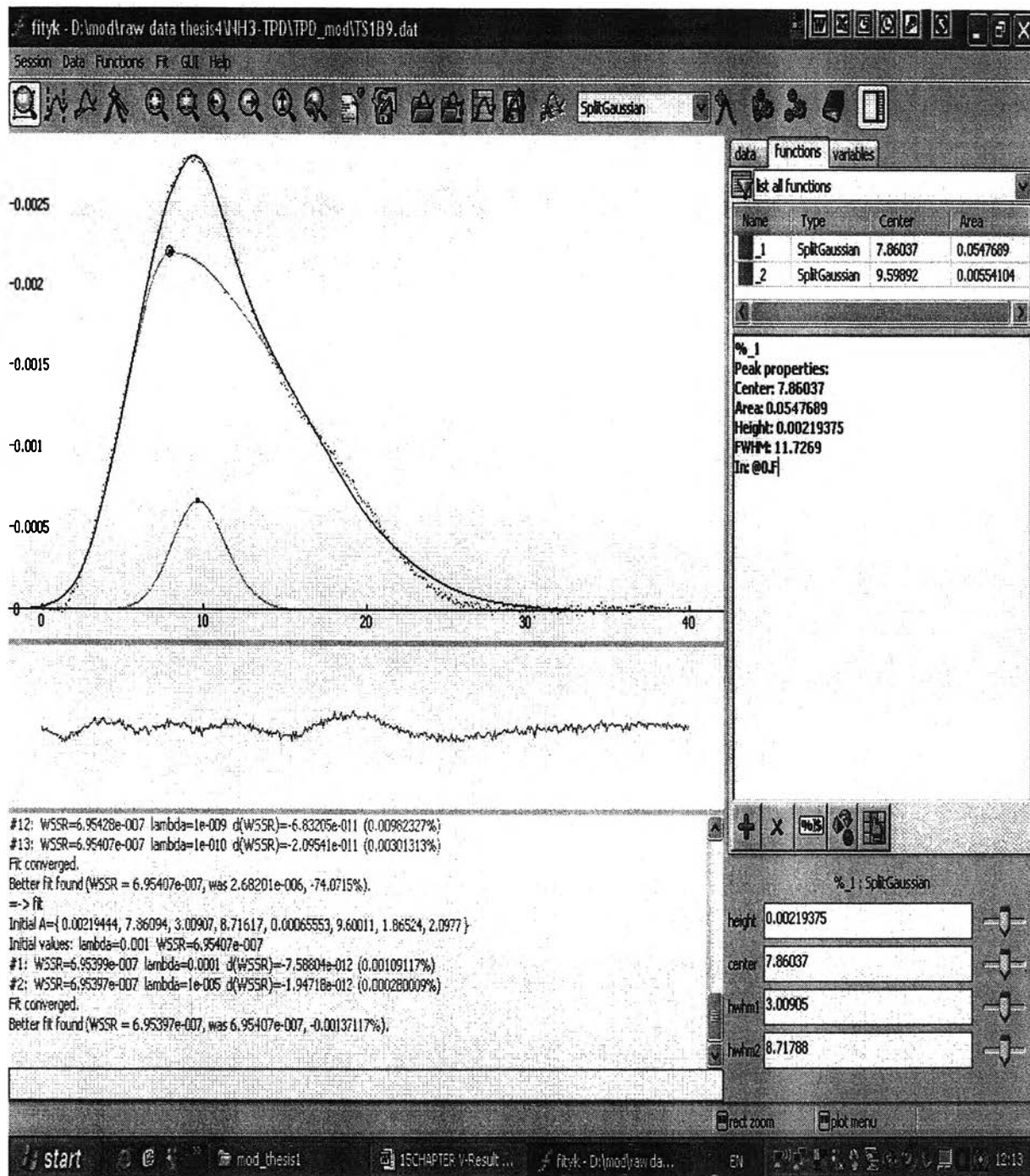**Figure 5.15** The data of peak fitting of Si/Ti = 22 as sample No.4 in table 5.4

Figure 5.16 The data of peak fitting of Si/Ti = 60 that pretreated with 5M HNO₃ as sample No.5 in table 5.4

Figure 5.17 The data of peak fitting of Si/Ti = 40 that pretreated with 5M HNO_3 as sample No.6 in table 5.4
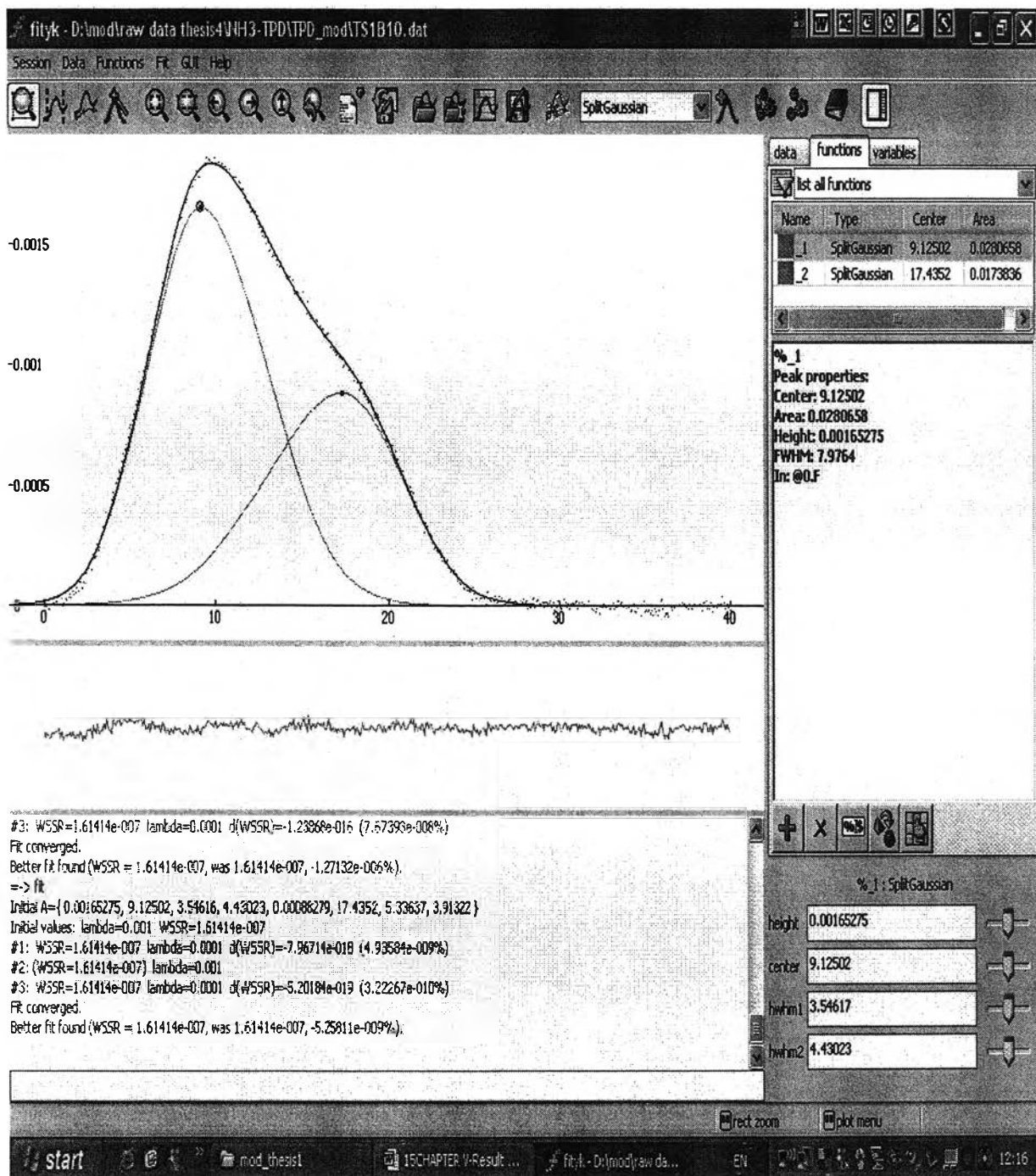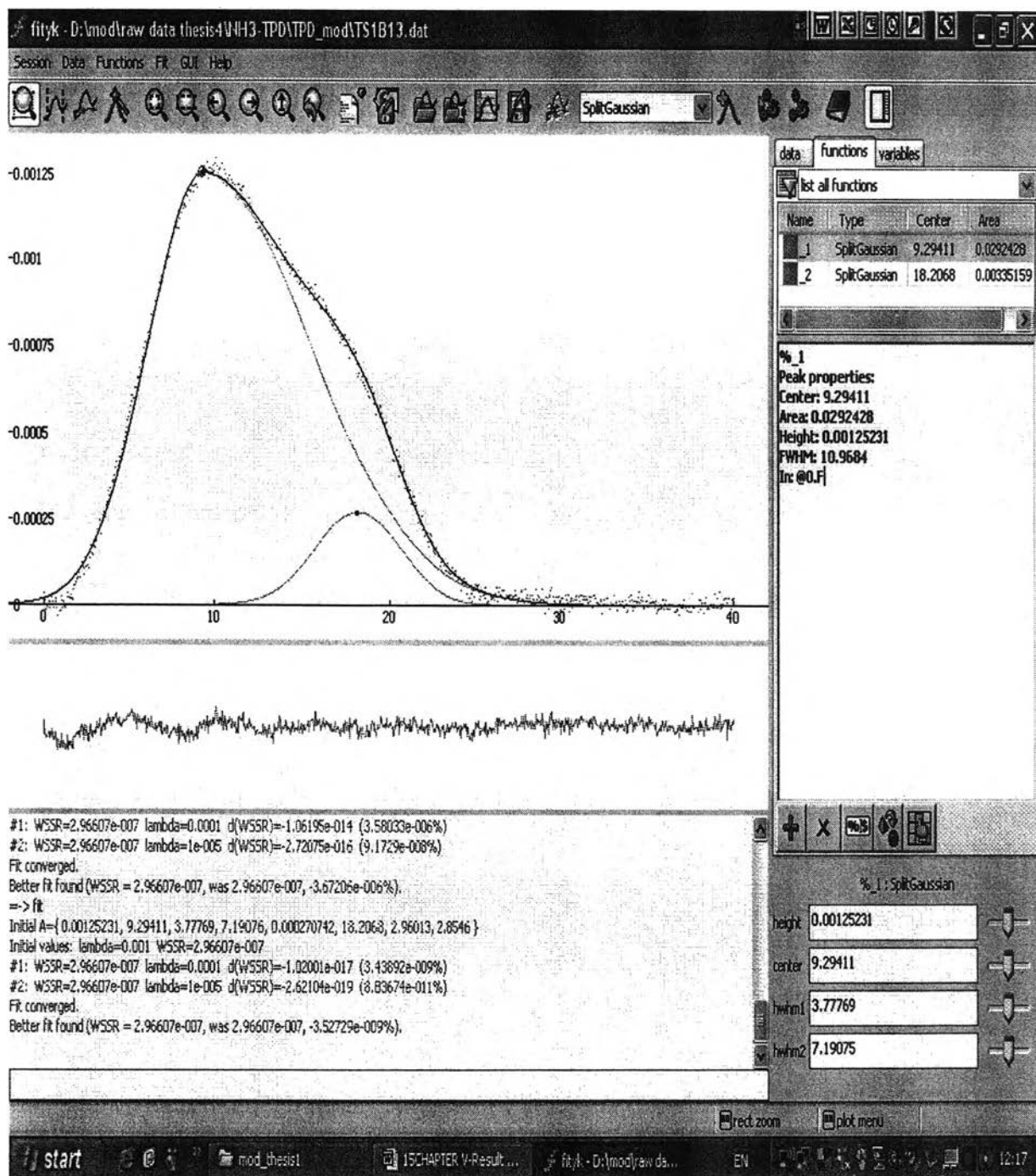
Figure 5.18 The data of peak fitting of Si/Ti = 32 that pretreated with 5M HNO_3 as sample No.7 in table 5.4

Figure 5.19 The data of peak fitting of Si/Ti = 22 that pretreated with 5M HNO_3 as sample No.8 in table 5.4

Figure 5.20 The data of peak fitting of Si/Ti = 40 that pretreated with 3M HNO$_3$ as sample No.9 in table 5.4

Table 5.4 Data of acid quantities and acid strength

| Sample No.	Time	Temp(°C)	Acid site (μmol/g)	Total (μmol/g)
1	9.13	133	110.4685	
	18.56	220	76.0860	186.5545
2	10.02	133	169.5576	
	19.91	225	19.5541	189.1112
3	9.13	140	169.5056	
	17.28	216	28.7303	198.2359
4	10.68	144	170.4736	
	20.52	235	18.1688	188.6424
5	9.17	133	63.6084	
	18.26	216	8.2668	71.8751
6	7.83	121	90.0285	
	9.69	136	9.4093	99.4378
7	7.85	119	123.9124	
	9.59	134	12.5364	136.4488
8	9.11	132	68.6073	
	17.28	207	42.4945	111.1018
9	9.29	133	67.4777	
	18.21	213	7.7337	75.2114

5.2 Catalytic reaction

This section reports the hydroxylation activity of TS-1 catalysts without and with pretreatment with NHO_3 solution. The results of catalysts without any pretreatment are reported in section 5.2.1. Section 5.2.2 discusses the effect of pretreatment on the hydroxylation activity of TS-1.

5.2.1 Effect of difference Si/Ti ratio

Figure 5.21 indicates that in the first 2 hours, the conversion of benzene of each catalyst increases with the reaction time. After that the activity of the sample Si/Ti = 60 remains constant at a value around 0.01%. The activity of the remaining three samples still keeps increasing. The catalytic activity of the sample Si/Ti = 22 reaches an upper limit after about 4 hours while the catalytic activity of the sample Si/Ti = 32 still increases for another 2 hours. After 6 hours, the activity of the sample Si/Ti = 40 still increases, though very slowly. The maximum benzene conversion achieves by the samples Si/Ti = 32 and Si/Ti = 40 is between 0.1-0.2%.

Taramasso *et al.*, 1983 reported that the TS-1 which had formula $xTiO_2.(1-x)SiO_2$ where x lies between between 0.01 and 0.025 exhibited the best hydroxylation activity. This was possibly due to an optimum amount of titanium existed in the framework. Out of this range, too low titanium in the framework or formation of non-framework titanium species might form. This would lead to the decrease in the hydroxylation activity. In our experiments, the samples Si/Ti = 32 and Si/Ti = 40 lie in the best suggested range. The difference among the amount of titanium framework of all the four samples, however, can not be determined from the infrared spectroscopy (the area of the band around 960 cm^{-1}). This may be because the technique used in our study is not sensitive enough to detect the difference or there are other unidentified factors affect the hydroxylation activity of the catalysts.

Since the sample Si/Ti = 40 exhibits the best performance among the samples investigated. The sample Si/Ti = 40 is, therefore, chosen to be further investigated by pretreatment with NHO_3 solution with different concentration.
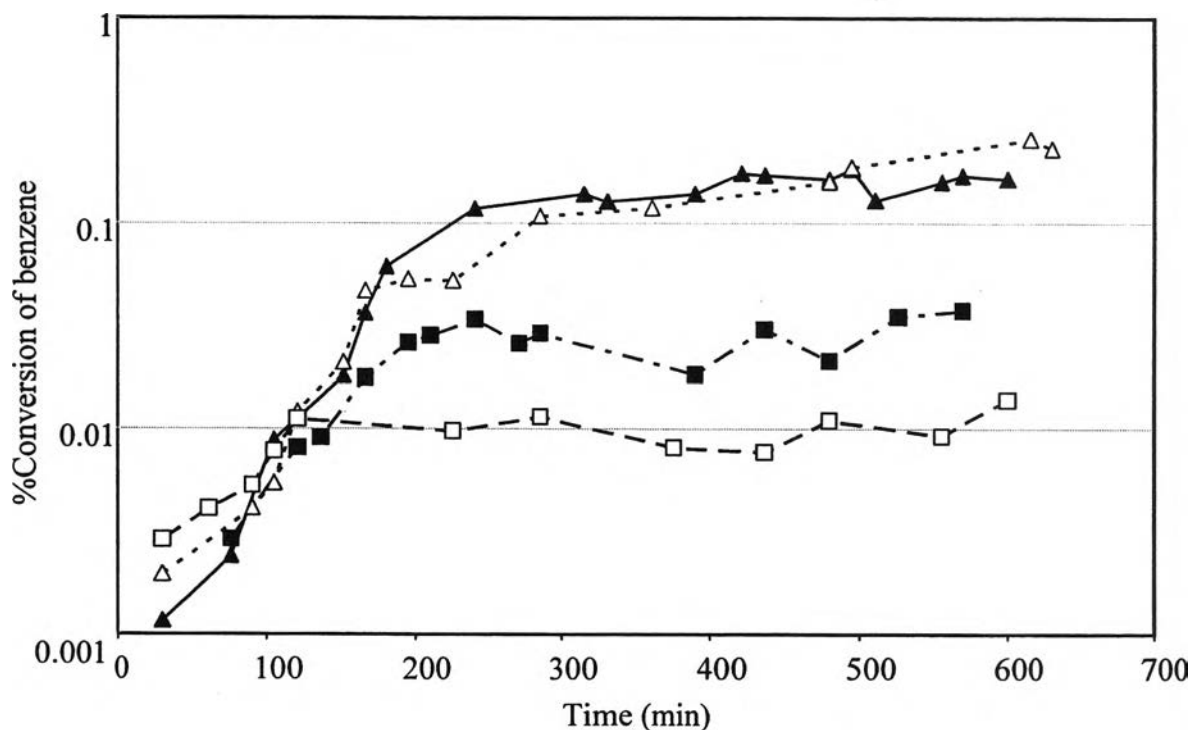
Figure. 5.21 The result of difference ratio of TS-1 catalysts in %conversion of benzene under periodic operation: Si/Ti = 60 (□) , Si/Ti = 40 (Δ) , Si/Ti = 32 (▲) , Si/Ti = 22 (■).

5.2.2 Effect of pretreatment

From section 5.2.1, the Si/Ti = 40 catalyst would be pretreated with HNO_3 solution and used for the hydroxylation of benzene. In this study, a Si/Ti = 40 catalyst sample was pretreated with 3M HNO_3 solution and another sample was pretreated with 5M HNO_3 solution. The hydroxylation activities of the catalysts without any pretreatment, pretreated with 3M and 5M HNO_3 are compared in Figure 5.22.

The experimental results in Figure 5.22 indicate the initial benzene conversions of catalysts are pretreated with 3M HNO_3 and 5M HNO_3 are higher than that of the unpretreat catalyst. The initial benzene conversion of the catalyst pretreated with 5M HNO_3 is slightly higher than the initial benzene conversion of the catalyst pretreated with 3M HNO_3. After 6 hours of operation, however, the benzene conversion profiles of all the catalysts merge altogether whether the catalyst is pretreated or not. This phenomenon suggests the unpretreat catalyst still undergoes some changing

during the reaction, as can be seen from the increase in the benzene conversion. This changing is likely the removal of some inactive structure(s) that hindrance the real active site. The inactive structure can be better removed by washing with HNO_3 solution. Therefore, the catalysts washed with HNO_3 solution performed high activity since the beginning of the operation period. The reduce of the inactive species can be seen from the UV-vis data (Table 5.2). The absorption at the wavelength about 270 nm, belongs to the six-folded coordinate titanium species – the inactive species that block the active sites [Li et al. (2001)], dramatically decreases after washing with HNO_3 solution. [Ref] also reported that this inactive species not only hindrance the hydroxylation reaction but also promoted the decomposition of H_2O_2. Thus, led to less amount of H_2O_2 to react with benzene. The removal of the inactive species allows the benzene reactant to gain access to the active site and allow more H_2O_2 to react with benzene. Therefore, the conversion of benzene increases.

The experiment also shows that higher acid concentration yields higher initial activity, but not so much. Since the washing with HNO_3 solution can dramatically incrase the initial benzene conversion, the pretreatment is also tried on the other samples. The pretreatment, however, was performed using only 5M HNO_3 solution. The hydroxylation activities of the Si/Ti = 60, 32 and 22 catalyst without and with pretreatment are illustrated in Figures 5.23-5.25, respectively.

The experimental results in Figure 5.23 indicates that the benzene conversion of the Si/Ti = 60 catalyst which are pretreated with 5M HNO_3 is higher than the unpretreated catalyst. The steady state benzene conversion increases from a value around 0.01% to another value around 0.02%. For the Si/Ti = 32 catalyst, when pretreated with HNO_3, the conversion of benzene becomes steady since the beginning of the experiment at a value around 0.1% [Figure 5.24], while the unpretreat catalyst has to take about 5 hours before reaching this steady state conversion level.

Figure 5.25 shows that the behaviour of the Si/Ti = 22 catalyst after the pretreatment is similar to the behaviour of the Si/Ti = 60 catalyst. The steady state benzene conversion of the pretreated Si/Ti = 22 catalyst becomes steady since the beginning of the reaction at a level around 0.1%, while steady state benzene conversion of the unpretreat sample stays at a lower level around 0.02%.

It should be noted here that after the pretreatment with 5M HNO_3, the samples Si/Ti = 22, 32 and 40 achieve the same level of benzene conversion at steady state, i.e. 0.1-0.2%, while the sample Si/Ti = 60 achieves a lower steady state benzene conversion, i.e. 0.02%. This finding suggests that the samples Si/Ti = 22, 32 and 40, though have different total titanium content, possess the same amount of tetrahedral coordinated titanium species (the active species for the hydroxylation of benzene). The different is the amount of the inactive six-fold coordinated titanium species in which the sample Si/Ti = 22 has the highest amount, follows by the samples Si/Ti = 32 and Si/Ti = 40, respectively. This is the reason why the sample Si/Ti = 22, before pretreatment, exhibits lower benzene conversion than the samples Si/Ti = 32 and 40. When the inactive titanium species is removed by acid washing, the number of accessible active hydroxylation sites of all 3 catalysts is about the same. The conversion of the 3 catalysts, therefore, is at the same level.

The sample Si/Ti = 60 has lower steady state benzene conversion than those 3 samples mentioned above though the catalyst is washed by HNO_3 solution because it possesses lower number of the active titanium species.

Another interesting phenomenon observed from the pretreatment experiment is the pattern the benzene conversion increases. For the samples Si/Ti = 32 and 40, it is found that the unpretreat catalysts can also gain the same conversion levels as of the pretreated catalysts. The reactant, H_2O_2, can also remove some inactive titanium species but take much longer time than washing with acid solution. For the Si/Ti = 22 catalyst, the amount of the inactive titanium species may be too high or too difficult to be removed by H_2O_2. Therefore, the steady state benzene conversion of the unpretreat catalyst is lower than the pretreated catalyst. Hence, we can conclude that washing with HNO_3 solution is more effective in removing the inactive titanium species than washing with H_2O_2. It is recommended to wash the catalyst by using HNO_3 solution before performing the hydroxylation of benzene in any future works that may occur.
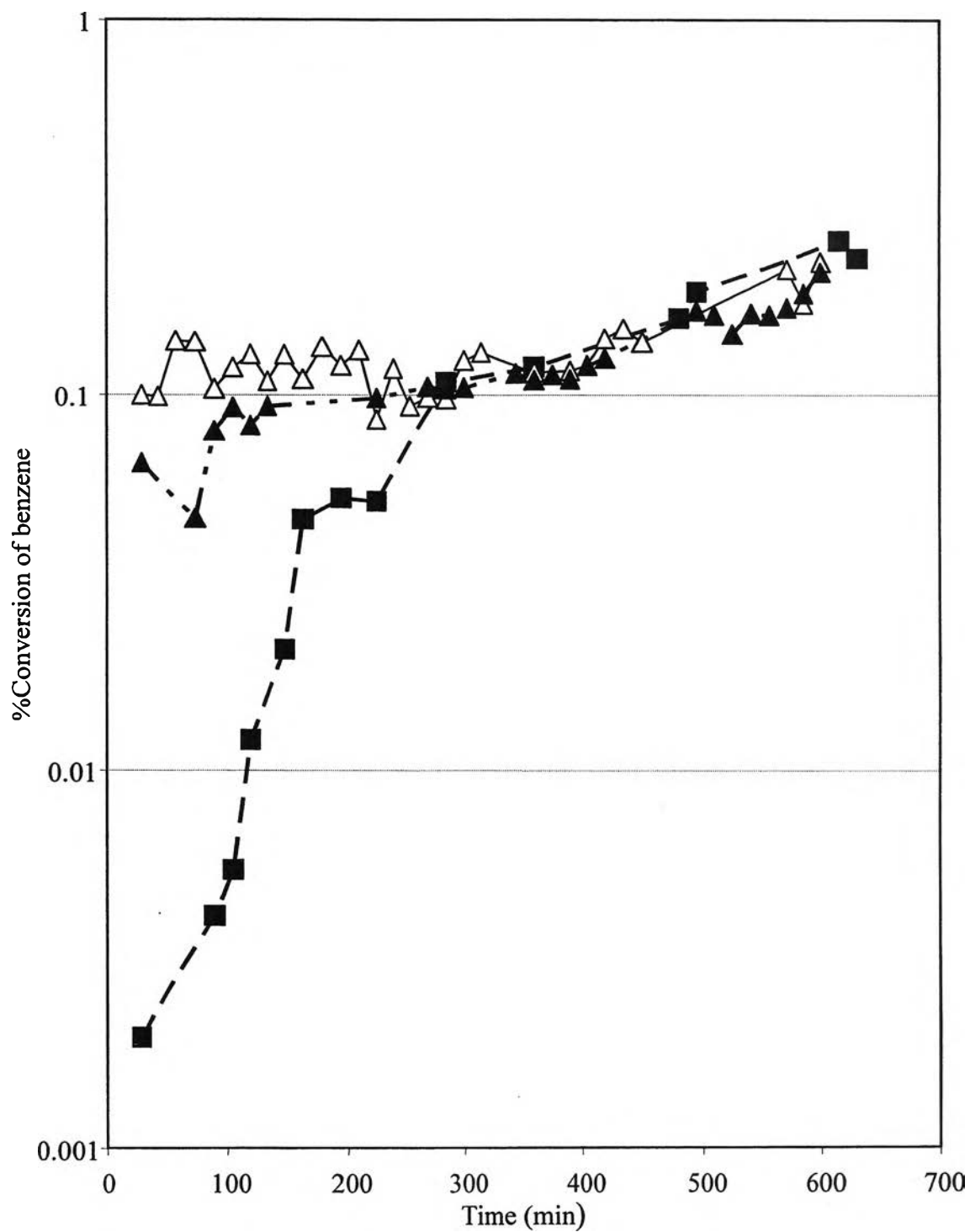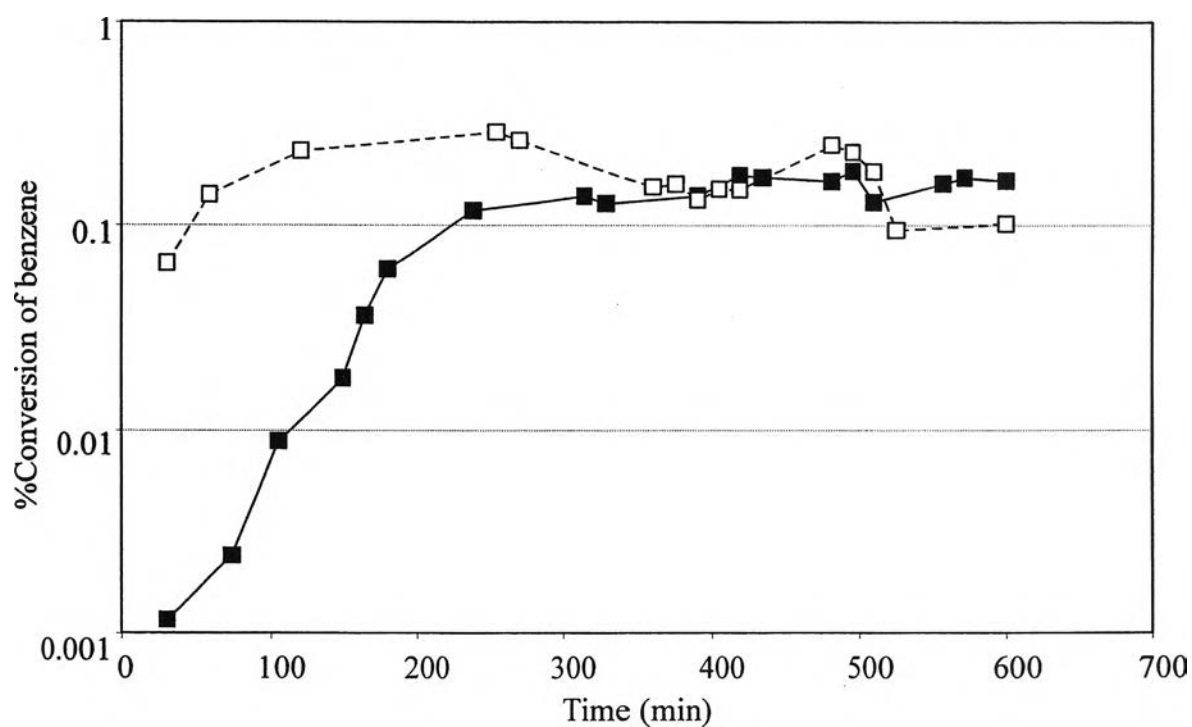
Figure 5.22 The effect of concentration of HNO_3 which pretreat Si/Ti ratio 40: pretreat with 3M of HNO_3 (▲) , pretreat with 5M of HNO_3 (Δ) and unpretreat (■).
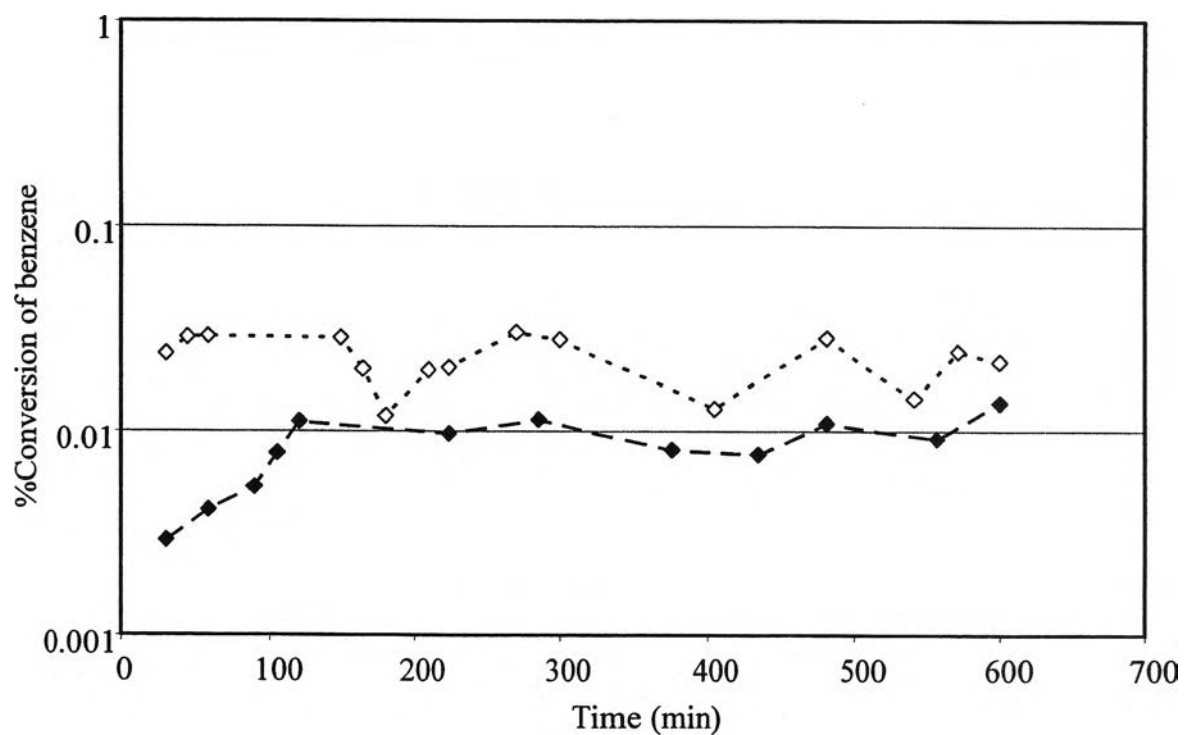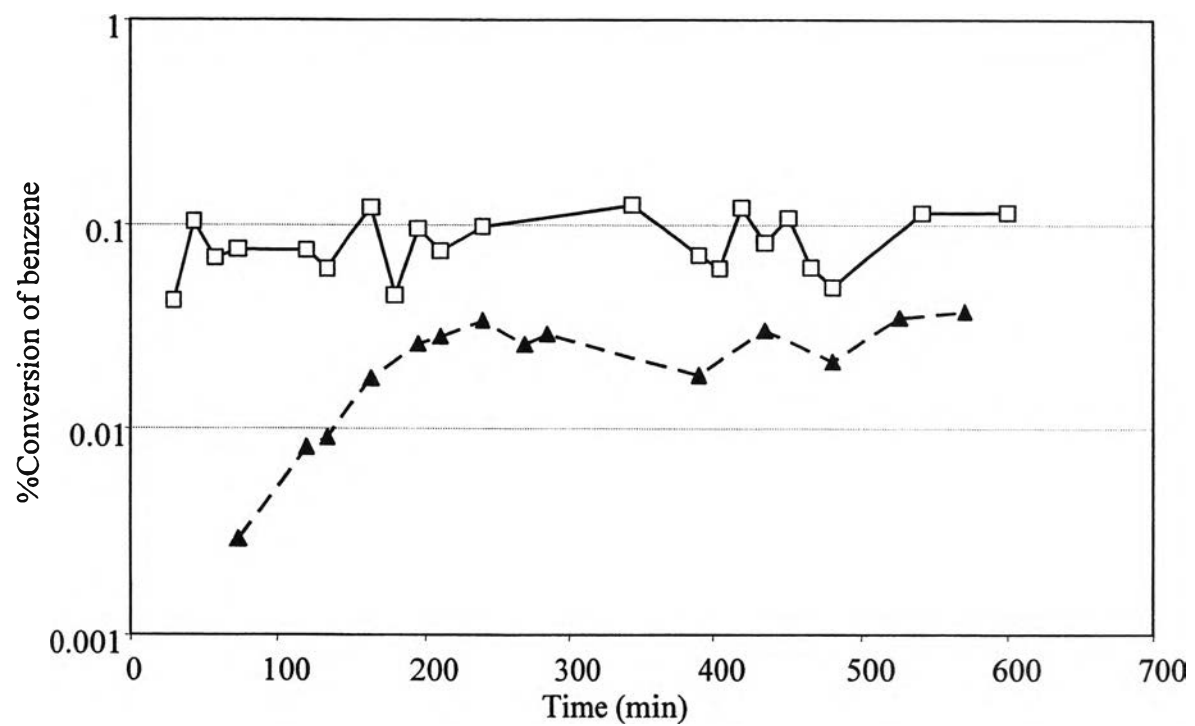
Figure 5.23 The effect of concentration of HNO_3 which pretreat Si/Ti ratio 60: unpretreat (▲), pretreat with 5M of HNO_3 (□).

Figure 5.24 The effect of 5M HNO_3 which pretreatment of Si/Ti ratio 32 (□) with unpretreatment (▲)

Figure 5.25 The effect of concentration of HNO_3 which pretreat Si/Ti ratio 22: unpretreat (▲) , pretreat with 5M of HNO_3 (□).